Electronic supplementary information

Luminescence sensing of weakly-hydrated anions in aqueous solution by self-assembled europium(III) complexes

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1. Experimental

Synthesis of ligand 2

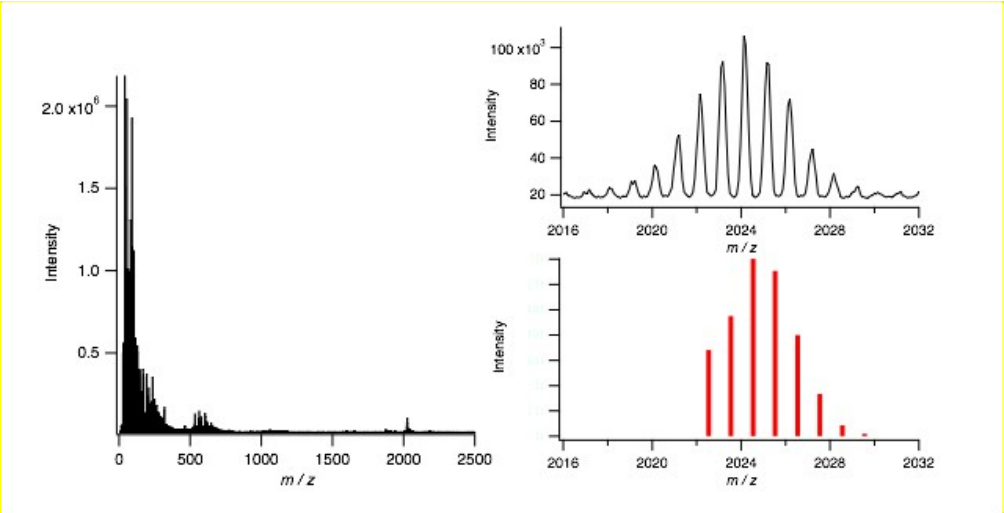
1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA, 400 mg, 1.00 mmol), *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′*N*′-tetramethyluronium hexafluorophosphate (HATU, 1.66 g, 4.4 mmol) and 1-hydroxy-7-azabenzotriazole (HOAt, 271 mg, 2.00 mmol) were dissolved in dry CH_2Cl_2/DMF (4:1) solvent (15 ml). The suspension was cooled to 0 °C using an ice bath and then *N,N*-diisopropylethylamine (DIPEA, 1.62 g, 12.5 mmol) was added. The mixture was stirred for 30 min under the N_2 atmosphere. Solid cholesterylamine (2.35 g, 6.09 mmol) was added and the solution was further stirred for 30 min at 0 °C, then stirred for 168 h at room temperature. The solution was diluted with CH_2Cl_2 (25 ml) and washed with 1 mol/L KOH (25 ml). From the water phase, the product was extracted with CH_2Cl_2 (10 ml × 6), and all CH_2Cl_2 solution was combined, dried over anhydrous K_2CO_3, and evaporated. The crude orange solid was reprecipitated from CH_2Cl_2/MeOH repeatedly. Finally, the solid was washed with a small amount of pentane to yield white solid (902 mg, 0.50 mmol, 49%).

^{1}H NMR ($CDCl_3$, 300 MHz, 298K) δ 0.68 (s, 12H), 0.80-2.30 (m, 160H), 2.73 (s, 16H, NC$\underline{H}_2$C$\underline{H}_2$N), 3.06 (s, 8H, NC$\underline{H}_2$CO), 3.60-3.80 (m, br, 4H), 5.32 (d, 4H, J = 3.4 Hz), 6.77 (d, 2.4H, J = 8.3 Hz, amide); Anal. Calcd. for $C_{124}H_{208}N_8O_4$•2.3 H_2O: C, 77.71; H, 11.18; N, 5.85. Found: C, 77.40 (–0.31%); H, 11.33 (+0.15%); N, 6.15 (+0.30%), HRMS (FAB, pos.): m/z = 1874.6403, $[C_{124}H_{208}N_8O_4 + H]^+$ requires 1874.6391.

Synthesis of [2Eu]Cl_3

Suspension of ligand **2** (90 mg) and $EuCl_3$•$6H_2O$ (0.95 equiv.) in dry EtOH (7 ml) was sealed in glass tube, followed by heating to 120 °C for 30 min under 50-120 W microwave irradiation. After removing the solvent, the residue was recrystallized from CH_2Cl_2 / 1,4-dioxane. The obtained solid was recrystallized from CH_2Cl_2 / CH_3CN to give yellowish xerogel-like solid. When the solid was strongly-colored, it was stirred with 30 mg of activated charcoal overnight in CH_2Cl_2 / MeOH before recrystalization.

Yield: 78%. Anal. Calcd. for $C_{124}H_{208}Cl_3EuN_8O_4$•$7H_2O$: C, 65.92; H, 9.90; N, 4.96, Found: C, 65.87 (–0.05%); H, 9.78 (–0.12%); N, 5.09 (+0.13%); MS (FAB, pos.): m/z = 2024 $[M–3Cl–2H]^+$.



Measurements

Negative-staining EM. The solution of [**2**Eu]Cl_3 in 20 wt% EtOH-H_2O was placed on a carbon-coated EM (200 mesh, treated with glow discharger) grid and left standing for 1 min at room temperature. The particles on the grid were negatively stained with 10 µl of 3% $La(OAc)_3$, dried under the incandescent lamp for 3 min after removal of excess stain with a filter paper, and observed by a transmission electron microscope (JEM1010, JEOL, Akishima, Japan) at 80 kV acceleration voltage. EM images were captured by a FastScan-F214 (T) charge-coupled device (CCD) camera (TVIPS, Gauting, Germany).

Dynamic light scattering (DLS). The solution of [**2**Eu]Cl_3 in 20 wt% EtOH-H_2O was put in a rectangular 1-cm pyrex cell. Light scattering measurements were performed at 25 °C on Malvern Zetasizer Nano ZS. Average data of 4 measurements per one sample was used.

Luminescence (phosphorescence) spectra and decay profiles were obtained with Perkin-Elmer LS-55 fluorophotometer (Xe flash lamp) at room temperature. Absorption spectra were measured on a JASCO V-670 spectrometer. Circular dichroism spectra were obtained with a JASCO J-820 spectropolarimeter. ^{1}H NMR spectra were measured with JEOL AV-300.

Microwave synthesis were done on CFM Discover Bench Mate (2450 MHz).

2. Luminescence lifetime measurements

(a) (b)

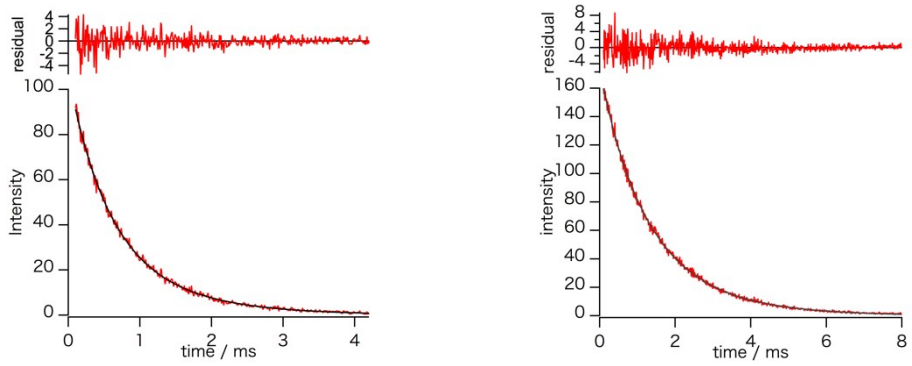


Table. Emission lifetime (τ / ms)[a] and hydration number (q)

τ_H (20 wt% EtOH-H_2O)	τ_D (20 % EtOD-D_2O)	q[b]	q[c]
0.545 ± 0.041	1.031 ± 0.086	0.40 ± 0.23	0.29 ± 0.19
1.06 ± 0.15	1.80± 0.17	–0.17± 0.12	–0.28 ± 0.17

Fig. S1 Emission decay profiles and lifetimes of [**2**Eu]Cl_3 in (a) 20 wt% EtOH-H_2O and (b) in 20 % EtOD-D_2O solvent. [**2**Eu]Cl_3: 5.0×10^{-5} M, bis-tris: 2.5×10^{-3} M, pH 7.0 (HCl), λ_{ex} = 260 nm, λ_{em} = 615 nm 25 °C, 1-cm quartz cell.

[a] Average value of 4 or 5 measurements.

[b] The q values were calculated using the equation[#]

$$q = 1.2 \times [\frac{1}{\tau_H} - \frac{1}{\tau_D} - (0.25 + 0.07 \times N_{amide})]$$ in H_2O

[c] The q values were calculated using the equation[*]

$$q = 1.2 \times [\frac{1}{\tau_H} - \frac{1}{\tau_D} - (0.32 + 0.075 \times N_{amide})]$$ in EtOH/H_2O = 20/80 (v/v)

, where N_{amide} is the number of amide bonds coordinating to the europium(III) center (N = 4 in our system), although the solvent effect in the self-assembly does not correctly match with the one used in the estimation of the parameters in this equation.

[#] A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc., Perkin Trans. 2*, 1999, 493.

[*] P. Dissanayake, Y. Mei and M. J. Allen, *ACS Catal.*, 2011, **1**, 1203; D. J. Averill and M. J. Allen, *Inorg. Chem.*, 2014, **53**, 6257.

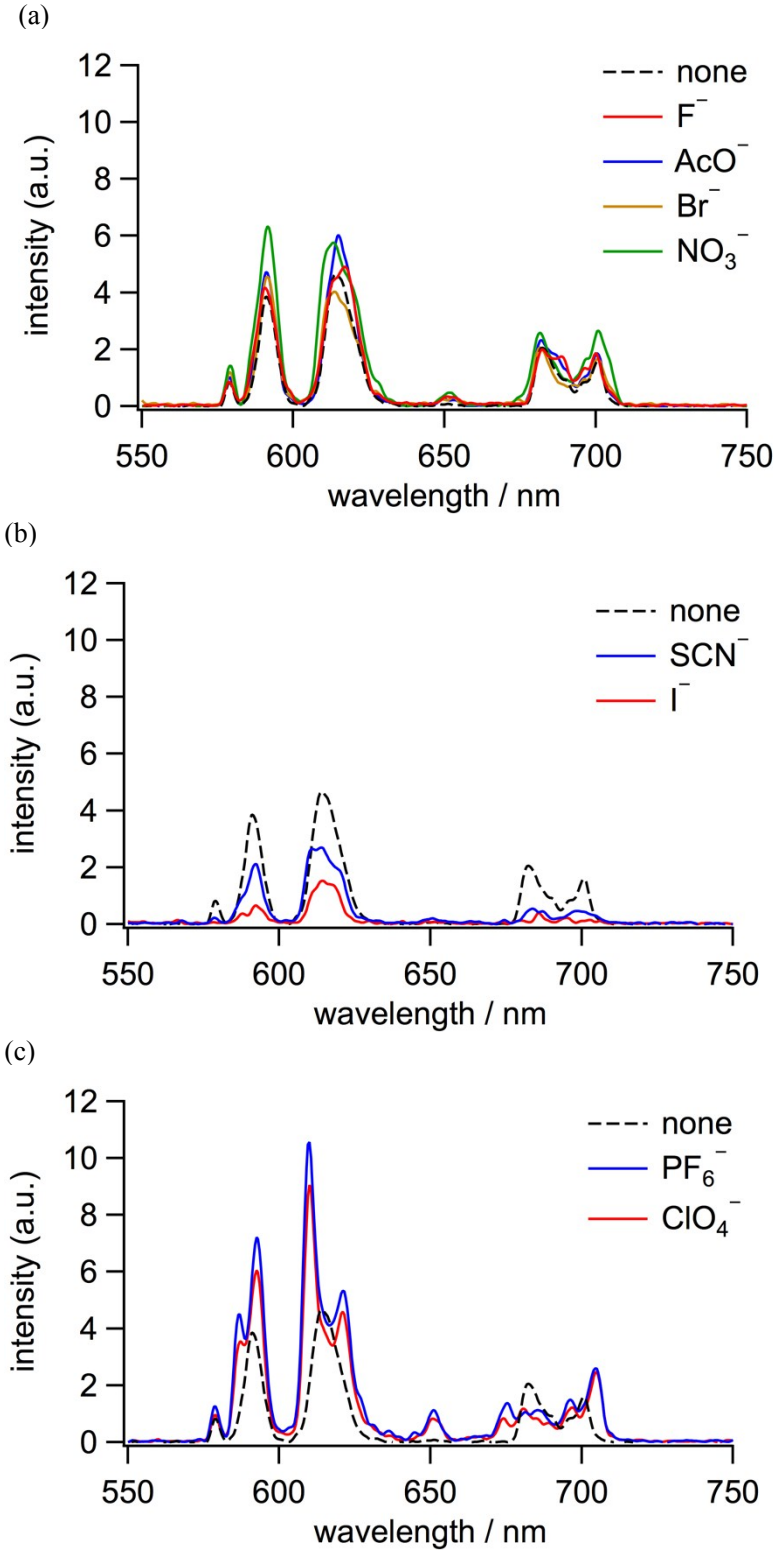


Fig. S2 Luminescence spectra of [**2**Eu]Cl_3 in the presence of 20 equiv. of NaX (X = anion). Black lines indicate the reference spectra without addition of anions., (a) X = F^-, AcO^-, Br^- and NO_3^-, (b) X= SCN^- and I^- and (c) X = ClO_4^- and PF_6^-. [**2**Eu]Cl_3: 5.0×10^{-5} M, [NaX]: 1.0×10^{-3} M in 20 wt% EtOH-H_2O (bis-tris: 2.5×10^{-3} M, pH = 7.0 (HCl), 25 °C, λ_{ex} = 260 nm, 1-cm quartz cell.

3. Characterization of nano particles

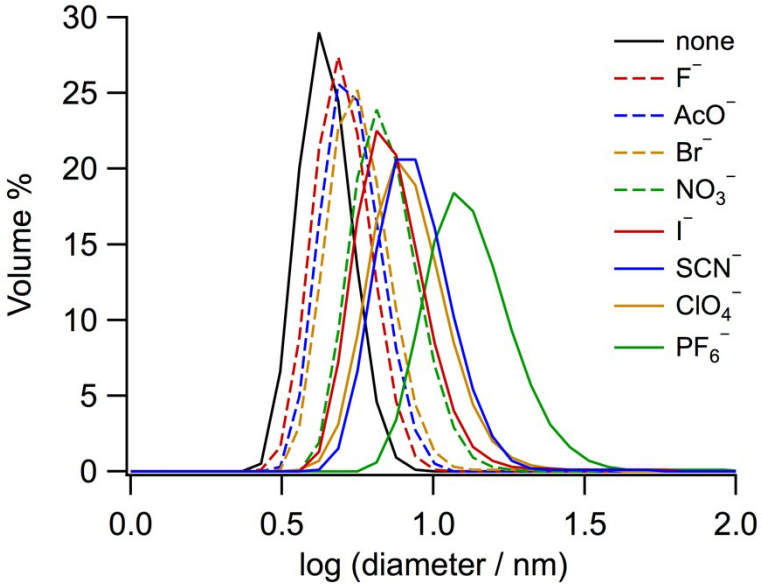


Fig. S3 Size distribution of [**2**Eu]Cl_3 in the presence of 20 equiv. of NaX by DLS measurements. X = $AcO^–$, $Br^–$, $NO_3^–$, $I^–$, $SCN^–$, $ClO_4^–$, and $PF_6^–$. [**2**Eu]Cl_3: $5.0 \times 10^{–5}$ M and NaX: $1.0 \times 10^{–3}$ M in 20 wt% EtOH-H_2O (buffer: $2.5 \times 10^{–3}$ M bis-tris, pH 7.0 (HCl)), 25 °C, 1-cm rectangular cell.

(a) (b)

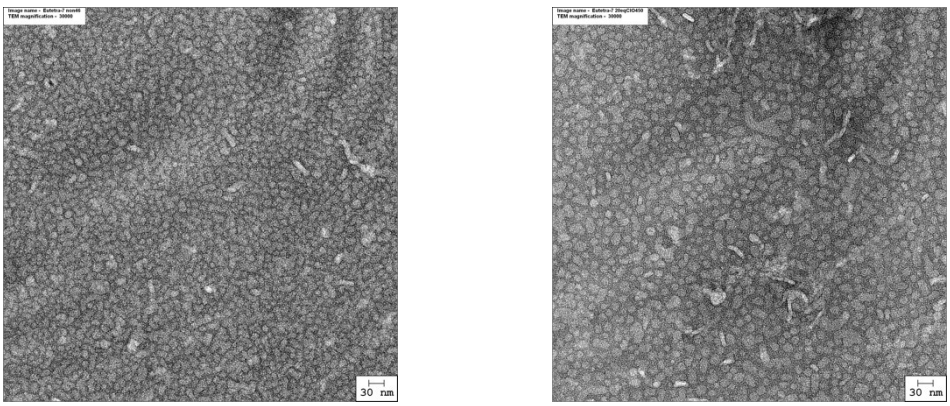


Fig. S4 TEM image (negative staining with 3% $La(OAc)_3$ aqueous solution) of (a) [**2**Eu]Cl_3 only and (b) in the presence of 20 equiv. of $NaClO_4$. [**2**Eu]Cl_3: $5 \times 10^{–5}$ M and $NaClO_4$: $1.0 \times 10^{–3}$ M in 20 wt% EtOH-H_2O (buffer: $2.5 \times 10^{–3}$ M bis-tris, pH 7.0 (HCl)), 25 °C.

4. Induced ciruclar dichroism of guest anions

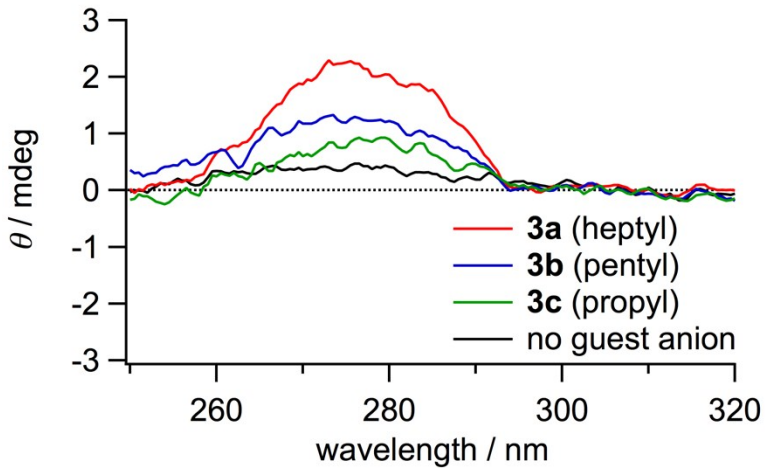


Fig. S5 Circular dichroism spectra of [**2**Eu]Cl_3 with guest sensitizers **3a**–**3c**. [**2**Eu]Cl_3: 5.0×10^{-5} M, [**3a**–**3c**]: 5.0×10^{-5} M in 20 wt% EtOH-H_2O, bis-tris: 2.5×10^{-3} M, pH = 7.0 (HCl), 25 °C, 1-cm quartz cell.

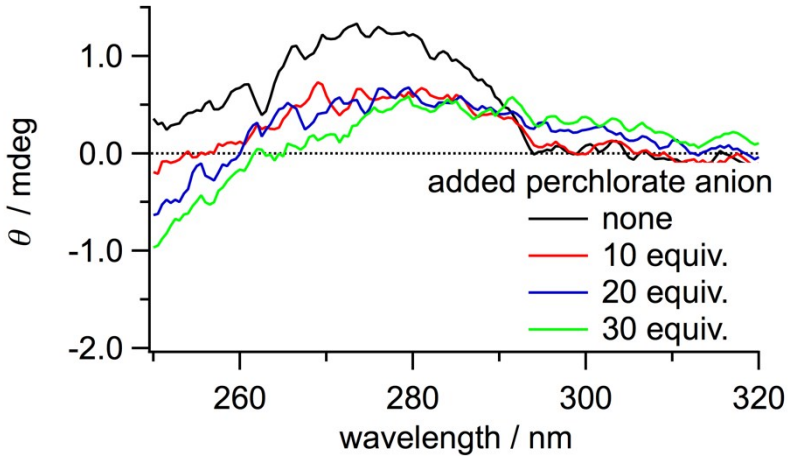


Fig. S6 Circular dichroism spectra of [**2**Eu]Cl_3 in the presence of guest sensitizers adding 0–30 eq of $NaClO_4$. [**2**Eu]Cl_3: 5.0×10^{-5} M and sensitizer (**3b**): 5.0×10^{-5} M in 20 wt% EtOH-H_2O (buffer: 2.5×10^{-3} M bis-tris, pH 7.0 (HCl)), 25 °C, 1-cm quartz cell.